

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 November 2004 (25.11.2004)

PCT

(10) International Publication Number
WO 2004/101952 A1

(51) International Patent Classification⁷: **E21B 33/13, C04B 28/00**

(21) International Application Number: **PCT/EP2004/005479**

(22) International Filing Date: 12 May 2004 (12.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 60/470,341 14 May 2003 (14.05.2003) US

(71) Applicant (for FR only): **SERVICES PETROLIERS SCHLUMBERGER [FR/FR]**; 42, rue Saint-Dominique, F-75007 Paris (FR).

(71) Applicant (for AT, AZ, DE, DK, IT, KP, KR, KZ, NO, NZ, PL, RO, RU, TM, UA, ZA only): **SCHLUMBERGER TECHNOLOGY B.V. [NL/NL]**; Parkstraat 83-89, NL-2514 JG The Hague (NL).

(71) Applicant (for GB, JP, NL only): **SCHLUMBERGER HOLDING LIMITED**; PO Box 71, Craigmuir Chambers, Road Town-Tortola (VG).

(71) Applicant (for CA only): **SCHLUMBERGER CANADA LIMITED [CA/CA]**; 525 - 3rd Avenue S.W., Calgary, Alberta T2P 0G4 (CA).

(71) Applicant (for all designated States except AT, AZ, CA, DE, DK, FR, GB, IT, JP, KP, KR, KZ, NL, NO, NZ, PL, RO, RU, TM, UA, ZA): **SOFITECH N.V. [BE/BE]**; Rue de Stall 140, B-1180 Belgium (BE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **LE ROY-DELAGE, Sylvaine [FR/FR]**; 15, rue Dulac, F-75015 Paris (FR).

WO 2004/101952 A1

(54) Title: **SELF ADAPTIVE CEMENT SYSTEMS**

(57) Abstract: A self-healing cement system includes cement, water and at least one additive that swells in contact with water from reservoir or from formation in the case of a structural failure in the set cement to provide a physical barrier in the zone of failure. Examples of such material include particles of super-absorbent polymer. These additives have the effect of making the cement self-healing in the event of physical failure or damage such as micro-annuli. The self healing property is produced by the contact of the water itself, the potential repair mechanism is thus activated if and when needed in case of start of loss of zonal isolation. Several super-absorbent polymers have been identified such as polyacrylamide, modified crosslinked poly(meth)acrylate and non-solute acrylic polymers.

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Self Adaptive Cement Systems

Technical Field of the Invention

[0001] The present invention relates to adaptive cement systems. In particular, the invention relates to cement systems which are "self-healing", i.e. system which can adapt to compensate for changes or faults in the physical structure of the cement, or which adapt their structure after the setting phase of the cement in the cementing of oil, gas, water or geothermal wells, or the like.

Background of the Invention

[0002] During the construction of underground wells, it is common, during and after drilling, to place a liner or casing, secured by cement pumped into the annulus around the outside of the liner. The cement serves to support the liner and to provide isolation of the various fluid-producing zones through which the well passes. This latter function is important since it prevents fluids from different layers contaminating each other. For example, the cement prevents formation fluids from entering the water table and polluting drinking water, or prevents water from passing into the well instead of oil or gas. In order to fulfill this function, it is necessary that the cement be present as an impermeable continuous sheath. However, for various reasons, over time this sheath can deteriorate and become permeable. The deterioration can be due to physical stresses caused by tectonic movements of temperature effects, chemical degradation of the cement, or various other reasons.

[0003] There have been a number of proposals to deal with the problems of deterioration of the cement sheath over time. One approach is to design the cement sheath to take into account physical stresses that might be encountered during its lifetime. Such an approach is described in US 6,296,057. Another approach is to include in the cement composition materials that improve the physical properties of the set cement. US 6,458,198 describes the addition of amorphous metal fibers to the cement slurry to improve its strength and resistance to impact damage. EP 1129047 and WO 00/37387 describe the addition of flexible materials (rubber or polymers) to the cement to confer a degree of flexibility on the cement sheath. WO 01/70646 and

PCT/EP03/01578 describe cement compositions that are formulated so as to be less sensitive to the effects of temperature on the cement when setting.

[0004] A number of proposals have been made for designs of self-healing concretes for use in the construction industry. These are described in US 5,575,841, US 5,660,624, US 5,989,334, US 6,261,360 and US 6,527,849, and in "Three designs for the internal release of sealants, adhesives, and waterproofing chemicals into concrete to reduce permeability", Dry, C. M., Cement and Concrete Research 30 (2000) 1969-1977. None of these are immediately applicable to well cementing operations because of the need for the cement to be pumpable during placement and because of the pressure and temperature range.

[0005] It is an objective of the present invention to provide well cementing systems that can be placed by pumping in the normal manner, and which contain materials that allow the cement sheath to adapt its structure in response to environmental conditions.

Summary of the Invention

[0006] More precisely, the present invention aims at providing well cementing systems that include at least one additive that reacts and/or swells when the set cement is in contact with an aqueous fluid, such as formation waters. This behavior has the effect of making the cement self-healing in the event of physical failure or damage.

[0007] The additive is a material which reacts/expands in contact with water – for instance from the underground formation which enters a fault in the cement matrix. Examples of such materials include super-absorbent polymers. Super-absorbent polymers are crosslinked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. When super-absorbent polymers absorb liquids, an elastic gel forms. The gel is a soft, deformable solid composed of water and the expanded polymer chains.

[0008] The polymer particles can be of almost any shape and size: spherical, fiber-like, ovoid, mesh systems, ribbons, etc., which allows their easy incorporation in cement slurries of comprising solid materials in discrete particle size bands. In practice, polymer particles ranging from about 10 to about 1500 μ can be used.

[0009] The absorbent materials are preferably dry blended with the cement and any other solid components before transport to the well-site, mixing with water and placement in the well. The sizes and quantities will be selected to allow even dispersion through the cement matrix.

[0010] It has been found that though the super-absorbent polymers such as polyacrylamide and modified crosslinked polymethacrylate swell when incorporated in a cement slurry, they seem to release at least part of the absorbed water during the cement hydration and hence, have a reserve of absorbability that allow them to swell again if they are later exposed to water due to a crack of the matrix for instance. Since they are highly reactive with water, the concentration of super-absorbent added to the blend must remain relatively small, compositions with more than 3.2% of super-absorbent (by weight of cement) may typically have a viscosity too high for pumping the slurry in favorable conditions. In fact the maximum SAP concentration depends on the slurry density and also on the nature of the Super Absorbent Polymer.

[0011] It has been found that the addition of salts such as sodium chloride or calcium chloride for instance favors the rheology of the systems thereby enabling increasing the concentration of super-absorbent polymers. Cement slurries of lower density have also a greater acceptability of higher concentrations of super-absorbent polymers, even without salt.

[0012] In another aspect of the present invention, at least part of the super-absorbent polymers are encapsulated so that they are – for instance in the form of a resin or other material that releases the polymer in response to exposure to a downhole parameter (for instance such as temperature, a specific mineral system, pressure, shear etc). In yet another aspect, the rupture of the encapsulating means is actually induced by the failure of the cement matrix, in a way similar to the mechanism described by Dry for instance in US 5,575,841, US 5,660,624, US 5,989,334, US 6,261,360 and US 6,527,849.

Detailed Description

[0013] A screening has been carried out for identifying super-absorbent polymers suitable for self-healing cementing applications. The main issues were to check the ability to dry blend the polymers with cement and to optimize the rheology and thickening time.

Testing procedure

[0014] Tests have been carrying out by incorporating powders of various types of polymers as solid additives in cement slurries. Properties of the slurry as well as properties of the set cement have been studied.

[0015] The slurries were optimized with the mere objective of obtaining stability. Focus was to get acceptable plastic viscosity (PV) and yield stress (TY) at mixing time and after 20 minutes of conditioning. Free water and sedimentation tests were also carried out. Mixing and test procedure was according to API Spec 10.

[0016] The same equipment and bob was used for all rheology measurements, whatever the tested design. Many tests were performed at one slurry density (15.8 lbm/gal) and one temperature (BHCT equal to 60°C). Some examples were studied at 12 lbm/gal and at 14 lbm/gal. For lowest density, the temperature is equal 25 °C and 85 °C. The design is based on tap water and black Dyckerhoff North cement. Unless otherwise mentioned, all designs include an antifoam agent based on polypropylene glycol at 0.03 gallon per US gallons per sack of 94 lbs of cement (in other words, 1 gps = 88.78 cc/kg), polynaphthalene sulfonate as dispersing agent at 0.04gps and the superabsorbent polymer at concentration ranging form 0.1% BWOC (by weight of cement) to 0.9% BWOC for 15.8 lbm/gal. Decreasing the density allows to increase the concentration in Super Absorbent Polymer. For instance for a given SAP the maximum concentration at 15.8 lbm/gal is 1% bwoc without salt in the mixing water and can reach 3 % bwoc at 12 lbm/gal.

[0017] Three types of superabsorbent polymers were tested: S1, a polyacrylamide available from Lamberti, Italy. Three grades were tested, namely S1G- Lamseal® G, with particles ranging form 500 µ to 1500 µ (density 1.25 g/cm³), S1GS – Lamseal® GS, with particles of about 200 µ (density 1.48g/cm³), and S1GM, Lamseal® GM, with particles of about 700 µ (density 1.47g/cm³). S2, a modified polyacrylate available from Itochu, Japan, under the name Aqualic® CS-6HM, selected for its salt resistance, in particular its capacity to keep super absorbent capacity in high valent metal ions solutions. The average particle size is 100µ and the density 1.46 g/cm³ . S3, a non soluble acrylic polymers , Norsocryl C200 from Atofina with particles of about 250 µ in average (density 1.6 g/cm³).

[0018] In the examples, bwoc or BWOC stands for by weight of cement and bwow or BWOW for by weight of water.

Experimental Results

Example 1: Addition Procedure

[0019] The first step was to define the best addition process. As shown in table 1 below, dry blending induces lower effects on rheology and free water and leads to an easy mixing

Table 1

Design	Reference	A1	A2	A3
S1G (% bwoc)		0.1	0.1	0.1
Note		prehydrated (static)	dry blended	prehydrated under agitation at 2000RPM during 15 minutes.
Mixing rheology				
Ty (lbf/100ft ²)	2.3	2.8	1.4	3.2
PV (cP)	25.5	18.9	27.2	32.4
BHCT rheology at 60°C				
Ty (lbf/100ft ²)	24.6	21.2	27.3	52.8
PV (cP)	20.9	18.4	26.6	33.3
10'1'gel	25/16	14/9	19/11	15/13
Free Water mL	1	7	trace	2.5
Sedimentation ppg	1.14	1	0.4	0.7

Example 2: Influence of the particle sizes

[0020] For the S1 particles, the finer the particles, the higher the rheology and free water.

Table 2

Design	Reference	S1 G	S1 GM	S1GS
S1 (% bwoc)		0.1	0.1	0.1
Mixing rheology				
Ty (lbf/100ft ²)	2.3	1.4	2.7	6.7
PV (cP)	25.5	27.2	29	41

BHCT rheology at 60°C				
Ty (lbf/100ft ²)	24.6	27.3	24.4	38.7
PV (cP)	20.9	26.6	35.6	40.9
10'/1'gel	25/16	19/11	15/12	12/9
Free Water mL	1	trace	2	4
Sedimentation ppg	1.14	0.4	1	0.9

Example 3:

[0021] This test shows that cement slurry with super-absorbent polymers S1 are compatible with conventional fluid loss control additive (flac). This shows that the composition of the present invention can still be optimized by the addition of conventional additives such as dispersing agent , fluid loss control agent, set retarder, set accelerator and anti-foaming agent.

Table 3

Design	X3.1	X3.2
S1G (% bwoc)	0.1	0.1
Flac		0.4
Mixing rheology		
Ty (lbf/100ft ²)	1.4	7.9
PV (cP)	27.2	104.7
BHCT rheology at 60°C		
Ty (lbf/100ft ²)	27.3	13.7
PV (cP)	26.6	125
10'/1'gel	19/11	13/7
Free Water mL	trace	trace

Example 4:

[0022] Results with the polymethacrylate based superabsorbent polymer S2 show less sensitivity to the addition mode.

Table 4.1

Design	Reference	X4.1	X4.2	X4.3	X4.4
S2 (% bwoc)		0.05	0.1	0.1	0.15
	-	dry blended	dry blended	prehydrated	dry blended
Mixing rheology					
Ty (lbf/100ft ²)	2.3	4.8	5.6	6.4	5.3
PV (cP)	25.5	31.9	35.9	37.9	64.8
BHCT rheology at 60°C					
Ty (lbf/100ft ²)	24.6	20.2	23.3	20.7	19.9
PV (cP)	20.9	24.3	22.4	30.3	57
10'/1'gel	25/16	17/9	15/9	12/7	12/10
Free Water mL	1		2.8	4.5	5.5
Sedimentation ppg	1.14	0.6	0.6	0.9	1

[0023] Polymer S2 can also be added in higher quantity, at least up to 0.45% BWOC as shown in the following table 4.2:

Table 4.2

Design	Reference	1	2	3	4
antifoam (gps)	0.03	0.03	0.03	0.03	0.03
Dispersing agent (gbs)	0.04	0.04	0.04	0.04	0.04
S2 (% bwoc)	0	0.9 (exces)	0.2	0.45	0.45
S2 (% bwow)	0	2	0.44	1	1
Remarque		dry blended	dry blended	dry blended	prehydrated
Mixing rheology					
Ty (lbf/100ft ²)	2.3	Too	8.3	19.7	24.9
PV (cP)	25.5	viscous	52.2	142.8	228.7
Comment					Difficult mixing
BHCT rheology at 60°C					
Ty (lbf/100ft ²)	24.6		14.3	25.8	11.6
PV (cP)	20.9	Too viscous	40.3	172.5	178.4
10'/1'gel	25/16		14/9	25/7	18/9
Free water mL	1	0	7	6	4.5
Sedim ppg	1.14	0.1	1.2	0.2	0.2

Example 5:

[0024] This example shows that the setting properties and the rheological properties can be optimized, a key requirement for well cementing applications. In all cases, the super-absorbent polymer was dry blended with the cement.

Table 5.1

Design		8	9	10
S2 (% bwoc)		0.1	0.1	0.1
Antifoam (gps)		0.03	0.03	0.03
Lignosulfonate (gps)		0.05	-	0.025
Fluid loss control agent (gps)		0.4	0.4	0.4
Polynaphthalene(gps)		0.045	0.045	0.045
Mixing rheology	Ty (lbf/100ft ²)	10.4	11	10.6
	PV (cP)	121.9	134	125.8
BHCT rheology at 60°C	Ty (lbf/100ft ²)	15.5	16.7	16
	PV (cP)	132	132.4	129
	10'/1'gel	24/10	9/5	12/7
	Free water mL	0	0	0
	Sedimentation ppg	0.2	0.2	0.4
	Thickening test 100 Bc (hh:min)	13h 30 min	3h 03 min	8h 49 min

Table 5.2

Design	29	30	31	32
Antifoam (gps)	0.03	0.03	0.03	0.03
Lignosulfonate (gps)	0.025	0.025	0.025	0.025
Fluid loss control agent (gps)	0.4	0.4	-	0.2
Polynaphthalene(gps)	0.045	0.6	0.045	0.045
Mixing rheology				
Ty (lbf/100ft ²)	46.8	41.9	23	32
PV (cP)	303	293	92	154
BHCT rheology at 60°C				
Ty (lbf/100ft ²)	32	35	6.6	19
PV (cP)	226	248	66	145
10'/1'gel	12/7	11/6	11/7	9/4
Free water mL	Trace	Trace	10	2.5

[0025] In the table 5.2, the designed slurries have a density of 15.8 lbm/gal, and the concentration of super-absorbent S2 is 0.3% bwoc (corresponding to 0.7% bwow).

Table 5.3

Design	33	34	35
Antifoam (gps)	0.03	0.03	0.03
Lignosulfonate (gps)	0.025	0.025	-
NaCl (by weight of water)			37
Fluid loss control agent (gps)	0.2	0.15	-
Polynaphthalene(gps)	0.045	0.045	0.9
Mixing rheology			
Ty (lbf/100ft ²)	46.8	45	4.4
PV (cP)	223	208	61
BHCT rheology at 60°C			
Ty (lbf/100ft ²)	27	50	14
PV (cP)	217	240	51
10'/1'gel	10/5	10/7	20/9
Free water mL	1.5	1	-
API Fluid loss (ml)		170	

[0026] In the table 5.3, the designed slurries have a density of 15.8 lbm/gal, and the concentration of super-absorbent S2 is 0.4% bwoc (corresponding to 0.9% bwow).

Example 6:

[0027] This example shows that the addition of a salt allows an increase of the concentration of superabsorbent polymer while keeping acceptable rheology properties. In table 6.1, tests have been carried out with sodium chloride as added salt. In table 6.2, the added salt is calcium chloride. In both tables, the cements have a density of 15.8ppg.

Table 6.1

Design	1	36	37	38
S2 (% bwoc)	0.9	0.9	0.9	0.9
Antifoam (gps)	0.03	0.03	0.05	0.05
NaCl (by weight of water)	0	37	18.5	37
Polynaphtalene(gps)	0.04	0.9	0.9	1.5
Mixing rheology				
Ty (lbf/100ft ²)	Too viscous	13.4	27.1	61.8
PV (cP)		119	207	352
BHCT rheology at 60°C				
Ty (lbf/100ft ²)		30.7	31.5	59
PV (cP)		107	1059	433
10'/1'gel		28/19	-	433
Free water mL		Trace		

Table 6.2

Design	70	81
Antifoam (gps)	0.05	0.05
Flac (gps)	0.5	-
Lignosulfonate (gps)	0.05	-
Polynaphtalene (gps)	-	0.9
Sulfonated melamine -formaldehyde (gps)	0.12	-
Sodium chloride (%BWOW)	-	37
Calcium chloride (%BWOC)	2	-
S2 (%BWOC)	0.45	0.9
Mixing rheology		
Ty (lbf/100ft ²)	29	30
PV (cP)	244	173
BHCT tests at 60°C		
Rheology		
Ty (lbf/100ft ²)	34	22
PV (cP)	211	110
10'gel/1'stiring	17/9	23/10
Free water (mL)	0	0
Fluid loss (mL API)	78	18
Thickening time	5h17min	-

Example 7:

[0028] This example shows that if the slurry density is lower, higher concentration of super-absorbent polymers can be used, even without the addition of a salt.

Design	X7.1	X7.2	X7.3
Density (lbm/gal)	14	12	12
BHCT (deg C)	60	25	85
Antifoam (gps)	0.03	0.02	0.02
Flac (gps)	0.4	-	-
Lignosulfonate (gps)	0.025	-	-
Polynaphthalene (gps)	0.045	0.03	0.03
S2 (%bwoc)	0.9	3	3
S2 (%bwow)	1.4	2.4	2.4
Mixing rheology			
Ty (lbf/100ft ²)	21.18	19.2	19.63
PV (cP)	156.9	90.3	86.39
Rheology at BHCT			
Ty (lbf/100ft ²)	49.31	27.5	4.92
PV (cP)	180.5	169.7	82.78
10'gel/1'stiring	32/22	28/12	11/6
Fluid loss (mL API)	-	149	240

Example 8:

[0029] Cement samples comprising super-absorbent polymers were taken from the sedimentation column and additional water was added at the surface of broken pieces to simulate contact with formation water after a crack. Tests were performed at room temperature and at 60°C. In all cases, swelling was observed showing that the super-absorbent polymer particles remain effectively available to absorb additional water (even though the cement matrix always comprises residual water).

Example 9:

[0030] This test was performed with super-absorbent S3. Good rheology is obtained.

Table9

Design	5	13	19
Density (lbm/gal)	15.8	15.8	15.8
BHCT (deg C)	60	60	60
Antifoam (gps)	0.05	0.03	0.05
Flac (gps)	0.5	0.4	-
Lignosulfonate (gps)	0.05	0.025	-
Polynaphthalene (gps)	-	0.05	0.9
Sulfonated melamine formaldehyde (gps)	0.12	-	-
Sodium chloride (%BWOW)	-	-	37
Calcium chloride (%BWOC)	2	-	-
S3 (%bwoc)	3	0.9	2
S3 (% bwow)	7.7	2.2	4.5
Mixing rheology			
Ty (lbf/100ft ²)	26	19	4
PV (cP)	262	195	54
BHCT Rheology			
Ty (lbf/100ft ²)	13	19	4
PV (cP)	154	145	30
10'gel/1'stiring	7/5	14/4	15/6
Free water (mL)	0	0	-
Fluid loss (mL API)	48	-	-

Claims

1. A composition for well cementing comprising a pumpable slurry of cement, water and a material having residual water-absorption properties after the setting of the cement, thereby susceptible to swell in contact with underground water in case of failure of the cement matrix.
2. The composition of claim 1, wherein said material is a super-absorbent polymer.
3. The cement system of claim 1, wherein the super-absorbent polymer is selected from the list consisting of polymethacrylate and polyacrylamide or a non-soluble acrylic polymers.
4. The cement system according to any of claims 2 to 3, wherein the super-absorbent polymer is added to the slurry dry-blended with the cement.
5. The cement system according to any of claims 2 to 4, wherein the super-absorbent polymer is added at a concentration between 0.05% and 3.2% by weight of cement..
6. The cement system according to claims 2 to 5 further comprising a salt.
7. The cement system of claim 6, wherein said salt is sodium chloride or calcium chloride.
8. The cement slurry according to claims 2 to 7, wherein the super-absorbent polymer is added under the form of particles ranging from 10 to 1500 μ .
9. The cement system according to any of the preceding claims, whereby the material is provided in a capsule that releases the material in response to exposure of the cement to at least one downhole parameter.
10. The cement system according to any of claims 1 to 9, whereby the material is provided in a capsule that releases the material when the cement matrix cracks.

11. The cement system according to any of the preceding claims further comprising at least one additive selected from the list consisting of dispersing agent, fluid loss control agent, set retarder, set accelerator and anti-foaming agent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/005479

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 E21B33/13 C04B28/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 E21B C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 200204 Derwent Publications Ltd., London, GB; Class A93, AN 2002-028940 XP002295616 & JP 2001 146457 A (DENKI KAGAKU KOGYO KK) 29 May 2001 (2001-05-29) abstract -----	1,2,5,6
X	DATABASE WPI Section Ch, Week 199209 Derwent Publications Ltd., London, GB; Class A93, AN 1992-072444 XP002296443 & ZA 9 100 876 A (SNASHALL H T) 24 December 1991 (1991-12-24) abstract ----- -/-	1,2,4,5

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed Invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed Invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the International search

Date of mailing of the International search report

16 September 2004

30/09/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Zimpfer, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/005479

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 271 350 A (AMERICAN CYANAMID CO) 13 April 1994 (1994-04-13) page 6 – page 9 -----	1-11
A	WO 01/74967 A (HEYING THEODORE L) 11 October 2001 (2001-10-11) page 4, line 5 – line 20 page 12 – page 13 -----	1-11
A	EP 0 530 768 A (HOECHST AG) 10 March 1993 (1993-03-10) page 3 – page 5 -----	1-11
A	US 4 664 816 A (WALKER CLARENCE O) 12 May 1987 (1987-05-12) column 4 – column 5 -----	9,10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2004/005479

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 2001146457	A	29-05-2001	NONE		
ZA 9100876	A	24-12-1991	NONE		
GB 2271350	A	13-04-1994	AU 657637 B2 AU 4610093 A CA 2105428 A1 DE 4329825 A1 FR 2695383 A1 JP 6218351 A ZA 9306517 A		16-03-1995 10-03-1994 05-03-1994 07-04-1994 11-03-1994 09-08-1994 11-10-1994
WO 0174967	A	11-10-2001	AU 4575001 A WO 0174967 A1 US 2002040812 A1		15-10-2001 11-10-2001 11-04-2002
EP 0530768	A	10-03-1993	AT 133928 T BR 9203431 A CZ 9202743 A3 DE 59205287 D1 EP 0530768 A1 ES 2083041 T3 JP 5201756 A MX 9205038 A1 US 5387626 A		15-02-1996 06-04-1993 17-03-1993 21-03-1996 10-03-1993 01-04-1996 10-08-1993 30-07-1993 07-02-1995
US 4664816	A	12-05-1987	NONE		